

Serial No. 10/016,562

**STATUS OF CLAIMS:**

Claims 1-23 are pending herein and are presented above for the convenience of the Examiner.

**REMARKS**

**A. Rejection of Claims 1-7, 9 and 10 under 35 U.S.C. 102**

Claims 1-7, 9 and 10 are rejected under 35 U.S.C. 102(e) as being anticipated by U.S. 2002/0076935 (Maex). Applicant respectfully traverses this rejection and its supporting remarks.

For example, independent claim 1 is directed to a method of etching a structure that comprises a first layer of undoped silicon oxide or F-doped silicon oxide and a second layer of C,H-doped silicon oxide. The structure is etched in a plasma-etching step, which is conducted using a plasma source gas that comprises nitrogen atoms and fluorine atoms, and which selectively etches the second layer of C,H-doped silicon oxide relative to the first layer of undoped silicon oxide or F-doped silicon oxide. Such a method is neither taught nor suggested by Maex.

The Office Action asserts that Maex describes a method that comprises providing a dielectric structure that comprises (a) a first dielectric layer such as undoped silicon oxide, and (b) a second organic low-k dielectric layer, such as BCB, FLARE or SILK, which is argued to correspond to the claimed layer of C,H-doped silicon oxide.

However, neither BCB nor FLARE nor SILK is a C,H-doped *silicon oxide* material as claimed. In fact, these materials are organic polymer layers. See, e.g., paragraph [0074] of Maex (emphasis added): "A first dielectric layer (12), i.e. an *organic polymer layer* comprising phenyl groups is formed on a substrate (11) ... Examples of such polymers are the benzocyclobutarenes, i.e. benzocyclobutene (BCB) commercially available as Cyclotene 5021™ poly arylene ether, i.e. FLARE™ II, aromatic hydrocarbon, i.e. SILK™, polyimides."

Nevertheless, the Office Action argues the following: "BCB is a low-k insulating material that contains Si, O, C, H (please see US 6,168,726, col. 3, line 12, cited in the IDS, for

Serial No. 10/016,562

further verification of its composition). This would form a low-k material with silicon oxide and C and H, which would read on [the] claimed C,H doped silicon oxide."

This assertion is respectfully traversed, for example, because one of ordinary skill in the art would immediately recognize that *silicon oxide* based materials, such as C,H-doped silicon oxide (e.g., Black Diamond<sup>TM</sup>), are in a class that is fundamentally distinct from organic polymer based materials, such as BCB.

For instance, U.S. Patent No. 6,168,726, cited in the Office Action, refers to two broad classes of low-k materials: (a) silicon-based materials, and (b) carbon-based materials. The '726 patent describes BCB (bivinyldisiloxane-benzocyclobutene), not as a silicon-based material, but rather as "*a carbon-based low-k material, ... which contains a few percent of silicon, but is otherwise an organic polymer including carbon, oxygen, and hydrogen. Like many other carbon-based dielectrics, BCB is spun onto the wafer in a liquid solvent and is then dried and cured to form the polymer.*" See, e.g., col. 3, lines 3-10. On the other hand, the '726 patent describes C,H-doped silicon oxide materials like those claimed (see, e.g., col. 3, line 46 to col. 4, lines 30 of the '726 patent as well as paragraph [0031] of the present specification) as silicon-based materials (see '726 patent, col. 8, lines 3-4).

See also the attached article, "A New CVD Process for Damascene Low *k* Applications," *Semiconductor Fabtech-10<sup>th</sup> Edition*, (June 1999), pp. 285-289, which further highlights the fundamental differences between (a) silicon-based films, and specifically silicon-oxide based films such as C,H-doped silicon oxide (e.g., Black Diamond<sup>TM</sup>) and carbon-based organic polymer films such as BCB, FLARE and SILK. For example, silicon-oxide based films, including C,H-doped silicon oxide (Black Diamond<sup>TM</sup>), have higher thermal stability and hardness relative to organic polymer films such as BCB, FLARE and SILK. Moreover, silicon oxide based films, including C,H-doped silicon oxide (Black Diamond<sup>TM</sup>), can be deposited by CVD and are thus readily integrated into existing process schemes using existing processing equipment, whereas organic polymer films such as BCB, FLARE and SILK are spun onto the wafer in a liquid solvent, increasing processing complexity.

The Office Action states that the prior response doesn't respond to Maex's teaching of etching the low-k layer such as BCB with nitrogen and fluorine atoms as presented in the rejection. It is respectfully submitted that this issue has now been addressed. BCB is not a C,H-

Serial No. 10/016,562

doped silicon oxide material as presently claimed, and one of ordinary skill in the art would recognize this to be the case.

In this regard, the Office Action also states that the plasma etching of the second dielectric layer, described by Maex, would have the same claimed selectivity to the first dielectric layer, because the plasma contains the same source gas as that of the claimed invention. However, due to the fundamental differences between carbon-based organic polymer materials such as BCB, FLARE and SILK, and silicon-oxide-based material such as the claimed C,H-doped silicon oxide, it would by no means follow that the selectivity claimed in connection with C,H-doped silicon oxide will be achieved with the BCB, FLARE and SILK materials taught in Maex.

Moreover, due to the similarity of the layers within the presently claimed structure (i.e., each of the claimed first and second dielectric layers is a silicon oxide based layer), it is respectfully submitted that the high levels of selectivity achieved in the present invention are unexpected.

For at least the above reasons, it is respectfully submitted that claims 1-7, 9 and 10 are neither anticipated by nor obvious in view of Maex.

**B. Rejection of Claims 8 and 12-20 under 35 U.S.C. 103(a)**

Claims 8 and 12-20 are rejected under 35 U.S.C. 103(a) as being unpatentable over Maex in view of U.S. Patent No. 6,573,187 (Chen). Applicants respectfully traverse this rejection and its supporting remarks.

In order to establish a *prima facie* case of obviousness under 35 U.S.C. 103, (a) there must be some suggestion or motivation to modify/combine the references of record, and (b) there must be a reasonable expectation of success. See MPEP §2143. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, not in applicant's disclosure. *Id.* The mere fact that references *can* be combined or modified does not render the resultant combination obvious unless the prior art also suggests the desirability of the combination or modification. MPEP 2143.01 (emphasis added) (citing *In re Mills*, 916 F.2d 680, 16 USPQ2d 1430 (Fed. Cir. 1990)).

As seen from the above discussion, Maex is deficient with respect to independent claim 1 (and with respect to independent claim 12 as well) at least in that it does not teach or suggest a

Serial No. 10/016,562

process in which one silicon oxide layer (in particular, a layer of C,H-doped silicon oxide) is selectively etched relative to another silicon oxide layer (in particular a layer of undoped silicon oxide or F-doped silicon oxide) using a plasma source gas that comprises nitrogen atoms and fluorine atoms. In fact, Maex teaches the use of an entirely different class of dielectric layers, i.e., carbon-based organic polymer films, in its etching step.

Chen does not make up for these deficiencies in Maex. The Office Action asserts that "Chen describes a method for forming a dual damascene structure having a via dielectric layer of undoped or F-doped silicon oxide 30 under a layer of C,H doped silicon oxide 32 such as Flare, Silk, or Black Diamond...".

In this regard, and as noted above, FLARE™ and SILK™ are organic polymers, rather than C,H doped silicon oxide materials as claimed. As to providing undoped or F-doped silicon oxide in combination with Black Diamond™ C,H doped silicon oxide, Chen merely teaches that dielectric layers 30 and 32 can contain "any suitable dielectric material such as SiO<sub>2</sub>, Fluorine doped SiO<sub>2</sub>, USG, FLARE, SILK or Black Diamond™ or any other suitable low-k dielectric material." See, e.g., col. 4, lines 28-35. Hence, Chen teaches nothing more than the fact that the two dielectric layers can be formed from *any* suitable low-k material. It is respectfully submitted that this vague general disclosure falls far short of teaching the desirability of providing a structure comprising a C,H doped silicon oxide layer (e.g., Black Diamond™) in combination with an undoped or F-doped silicon oxide layer as presently claimed, and certainly not in a process like that claimed in which such a structure is etched using a plasma source gas that comprises nitrogen atoms and fluorine atoms, which plasma source acts to selectively etch the second layer of C,H-doped silicon oxide relative to the first layer of undoped silicon oxide or F-doped silicon oxide.

Indeed, to the extent that one of ordinary skill in the art would be motivated to follow the teachings of Maex regarding etching chemistry (as asserted in the Office Action), it is respectfully submitted that the teachings of Maex regarding selection of organic polymer dielectric materials such as FLARE or SILK would likewise be followed.

Finally, even assuming solely for the sake of argument that Chen did somehow provide motivation to substitute the C,H-doped silicon oxide layer taught therein (specifically, the Black Diamond™ material) for the carbon-based organic polymer materials (specifically, the BCB, FLARE and SILK materials) taught in Maex, it is respectfully submitted that there would be no

Serial No. 10/016,562

reasonable expectation of success associated with this substitution, due to the radical differences that exist between the carbon-based organic polymer materials taught in Maex and the C,H doped silicon oxide layers taught in Chen.

Stated from the perspective of the present invention, due to the similarity of the layers within the presently claimed structure (i.e., both of the claimed layers are silicon oxide based layers), it is respectfully submitted that the high levels of selectivity achieved in the present invention are unexpected.

For at least these reasons, it is respectfully submitted that independent claims 1 and 12 are unobvious over Maex in view of Chen.

Claims 8 and 13-20, which depend directly or indirectly from either claim 1 or claim 12, are also unobvious over Maex in view of Chen for at least the same reasons.

Accordingly, reconsideration and withdrawal of the outstanding rejection of claims 8 and 12-20 under 35 U.S.C. 103(a) are respectfully requested.

**C. Rejection of Claims 11 and 21 under 35 U.S.C. 103(a)**

Claims 11 and 21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Maex in view of Chen and further in view of U.S. Patent No. 6,194,128 (Tao). Applicants respectfully traverse this rejection and its supporting remarks.

First, the Office Action asserts that it "would have been obvious ... to etch a C,H-doped oxide using MERIE system since it is RIE system and Maex describes that the plasma etch includes RIE..." However, as noted above, the BCB material of Maex is not a C,H-doped silicon oxide. Moreover, no motivation is given for discarding the RIE system of Maex and utilizing a MERIE system, other than the fact that both are RIE systems.

Furthermore, as noted above, Maex and Chen are deficient with respect to independent claims 1 and 12 at least in that these references do not teach or suggest a process in which one silicon oxide layer (in particular, a layer of C,H-doped silicon oxide) is selectively etched relative to another silicon oxide layer (in particular a layer of undoped silicon oxide or F-doped silicon oxide) using a plasma source gas that comprises nitrogen atoms and fluorine atoms.

Tao does not make up for these deficiencies in Chen and Maex. For example, Tao at col. 5, lines 41-46 and col. 6, lines 48-51 teaches the formation of a dielectric layer of  $\text{SiO}_{3/2}\text{H}_{1/2}$ , or of carbon-based low-k dielectrics (e.g., FLARE™, discussed above, or PAE-II) by spin coating.

Serial No. 10/016,562

For at least the above reasons, it is respectfully submitted that independent claims 1 and 12 (and claims 11 and 21 dependent thereon) are unobvious over Maex, Chen and Tao.

Accordingly, reconsideration and withdrawal of the outstanding rejection of claims 11 and 21 under 35 U.S.C. 103(a) are respectfully requested.

**C. Rejection of Claims 22 and 23 under 35 U.S.C. 103(a)**

Claims 22 and 23 are rejected under 35 U.S.C. 103(a) as being unpatentable over Maex in view of U.S. Patent No. 6,245,690 (Yau) or alternatively Maex and Chen in view of Yau. Applicants respectfully traverse this rejection and its supporting remarks.

The Office Action asserts that "it would have been obvious for one skill[ed] in the art at the time of the invention in light of Yau's teaching of using plasma-assisted CVD process in order to deposit organic low-k material such as C-H doped silicon oxide with reasonable expectation of success." This assertion is respectfully traversed.

First, as noted above C,H-doped silicon oxide is not an "organic low-k material." Moreover, as also noted above, Maex and Chen are deficient with respect to independent claims 1 and 12 at least in that these references do not teach or suggest a process in which one silicon oxide layer (in particular, a layer of C,H-doped silicon oxide) is selectively etched relative to another silicon oxide layer (in particular a layer of undoped silicon oxide or F-doped silicon oxide) using a plasma source gas that comprises nitrogen atoms and fluorine atoms. Yau does not make up for this deficiency in Maex and Chen.

Indeed, as noted above, to the extent that one of ordinary skill in the art would have been motivated to follow the teachings of Maex regarding etching chemistry, it respectfully submitted the teachings of Maex regarding selection of carbon-based organic polymer films such as BCB, FLARE and SILK would likewise have been followed. As noted above, such organic polymer films are spun on in a liquid solvent and is then dried and cured. In contrast, it is noted that Yau is described in U.S. Patent No. 6,168,726 as relating to the CVD deposition of Black Diamond™ C,H-doped silicon oxide material (see, e.g., col. 3, line 47 to col. 4, line 30 of U.S. Patent No. 6,168,726), rather than organic polymer films such as BCB, FLARE and SILK.

For at least the above reasons, it is respectfully submitted that independent claims 1 and 12 (and claims 22 and 23 dependent thereon) are unobvious over Maex, Chen and Yau.

Serial No. 10/016,562

Accordingly, reconsideration and withdrawal of the outstanding rejection of claims 22 and 23 under 35 U.S.C. 103(a) are respectfully requested.

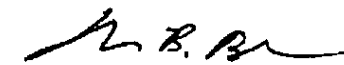
### **CONCLUSION**

Applicants submit that all pending claims of the present invention are in condition for allowance, early notification of which is earnestly solicited. Should the Examiner be of the view that an interview would expedite consideration of this Amendment or of the application at large, request is made that the Examiner telephone the Applicant's attorney at (703) 433-0510 in order that any outstanding issues be resolved.

### **FEES**

The Commissioner is authorized to charge any fees due and owing in respect to this amendment to deposit account number 50-1047.

Respectfully submitted,




David B. Bonham  
Registration No. 34,297

Attorney for Applicant  
Mayer Fortkort & Williams, PC  
251 North Avenue West, 2<sup>nd</sup> Floor  
Westfield, NJ 07090  
Tel.: 703-433-0510  
Fax: 703-433-2362

#### **Certificate of Facsimile Transmission**

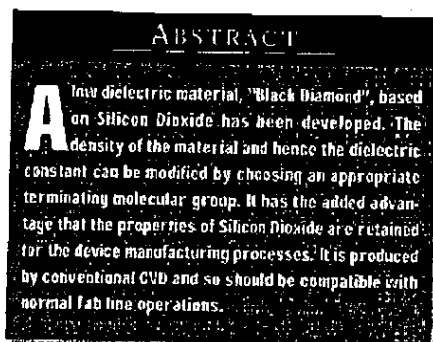
I hereby certify that this document and any document referenced herein is being sent to the United States Patent and Trademark office via Facsimile to: 703-872-9311 on June 4, 2004.

David B. Bonham  
(Printed Name of Person Mailing Correspondence)

  
(Signature)

# A New CVD Process For Damascene Low k Applications

BEN PANG, WAI-FAN YAU, PETER LEE & MENDI HAIK, *Applied Materials Inc., Santa Clara, CA, USA*



## INTRODUCTION

Recently, several IC companies have announced plans for devices with copper wiring using damascene integration. The first generation of these devices will use silicon oxides for the inter-metal dielectric layers. To further reduce the RC delay in these devices, it is clear that low  $k$ /cu damascene structures are needed. According to the SIA roadmap, very low  $k$  materials ( $k < 3.0$ ) are required for volume production by 2002. While most low  $k$  materials have mainly addressed the needs of aluminum gap fill applications, a new product, called Black Diamond, has been specifically developed for cost-effective, low  $k$  damascene applications.

## ORGANIC VS. INORGANIC MATERIALS

First-generation low  $k$  materials have generally followed an evolutionary approach by modifying silicon oxides to achieve reduced dielectric constants. The best examples are Fluorine-doped silicate glass (FSG) and hydrogen silsesquioxane (HSQ). Some of the initial low  $k$  materials were based on spin on technology and generally faced two hurdles: 1) lack of device integration knowledge on these new materials (particularly organic polymers), and 2) complicated and expensive manufacturing sequences for these new materials. FSG has been implemented into production at several sites with relatively smooth integration and a  $k$ -value of approximately 3.5.

For the second-generation of low  $k$  films, with dielectric constants below 3.0, various organic polymers, such as BCB, are being investigated. A new silicon-based film, called Black Diamond, is deposited using proven

Property	Inorganic (FSG, HSQ)	Organic (BCB, BCB)	Low $k$ Material (Black Diamond)
Dielectric Constant	~3.5	~2.8	~2.8
Thermal Stability	Good	Good	Good
Adhesion	Good	Good	Good
Chemical Resistance	Good	Good	Good
Process Compatibility	Good	Good	Good
Cost	Low	High	Low
Environmental Impact	Low	High	Low
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good
Integration	Good	Good	Good
Reliability	Good	Good	Good
Scalability	Good	Good	Good
Manufacturability	Good	Good	Good
Performance	Good	Good	Good



## BLACK DIAMOND DIELECTRIC

The dielectric constant of a specific material has three main contributors: electronic, ionic, and orientation. The electronic contribution represents the response of the electrons to an applied electric field and is related to the number of bonds per unit volume. Therefore, for a fixed class of materials, the electronic contribution is directly related to the density of the material. The ionic contribution represents the response of the atoms to an applied electric field. It is related to the types of atoms (Si, C, O, N, H, F, etc) present in the material. The orientation contribution represents molecular response to an applied electric field and is related to the structure of the material.

There are two primary approaches for achieving low dielectric constant materials. The first approach is to lower the electronic contribution. The second approach is to lower the orientation contribution and/or the ionic contribution. The first approach is represented by low density materials such as Black Diamond, HSQ, Xerogel and Aerogel. The second approach is repre-

TABLE 2. BOND ENERGY  
FOR TERMINATING GROUPS

THE UNIVERSITY OF CHICAGO

### TABLE 3. SUMMARY OF BLACK DIAMOND FILM PROPERTIES

The image is a high-contrast, black-and-white scan of a textured surface, likely the cover or endpaper of an old book. The texture is dense and grainy, with a mottled appearance of dark and light areas. A prominent dark, horizontal band runs across the top of the image, possibly representing the spine or a binding edge. The overall composition is abstract due to the extreme contrast and noise inherent in the scan.

~~sented by polymeric materials such as Amorphous Fluorinated Carbon, Parylene, BCB, Flare, and SiLK.~~

Black Diamond is a low density silicon dioxide-like material formed by a Chemical Vapour Deposition method. The lower density is achieved by introducing network terminating species into the Si-O matrix. The precursors used include a silicon-containing compound, typically an organosilane ( $\text{R-SiH}_3$ ), and an oxidizer. A simplified reaction mechanism is as follows:

1. Partial oxidation of the organosilane in the gas phase
2. gas phase reaction of partially oxidized organosilane species to form a complex nucleus
3. adsorption of complex nucleus arriving at the wafer surface
4. adsorbed complexes aggregate to form a Black Diamond film on the wafer.

The density of the material, hence  $A$ , can be modulated at each phase in the reaction as well with the appropriate choice of the R (network terminating group). In general, a larger terminating group can give rise to a lower overall density. Because the organic component functions as a network terminating group (SI-R) and is not part of the C-Si-O network, Black Diamond maintains the material advantages of a silicon oxide base film.

The partial oxidation reaction and surface reaction conditions must also be optimized depending on the choice of the network terminating group. The oxidation of these species depends on the bond energy and the oxidation environment.

The Black Diamond family of low  $k$  products has been developed on conventional parallel plate single-wafer CVD chamber technology and uses proven CVD concepts. The first product is a silicon oxide-based low  $k$  film specifically for 0.13 $\mu$ m generation low  $k$ /copper damascene technology. All precursors are semiconductor grade, non-proprietary gaseous chemicals. The film can achieve a bulk dielectric constant of 2.5-2.7, and integrated IMD stack dielectric constant of  $\leq 3.0$ . By maintaining the adhesion, thermal, and mechanical properties of silicon oxide, this film provides an evolutionary path from Cu/oxide to Cu/low  $k$  device designs. A second-generation product with  $k=2.4$  is under development for extension to 0.10 $\mu$ m devices.

## FILM PROPERTIES

Because the film contains primarily silicon and oxygen, Black Diamond retains many of the beneficial thermal and mechanical properties of silicon oxide (Table 3 shows a summary of film properties). The glass transition temperature is well above 450°C and isothermal weight loss is <1%wt per hour at 450°C, Figure 1. Reduction of the dielectric constant is achieved primarily through maximizing the free volume in the microstructure.

One concern for low *k* materials is decreased mechanical strength. As shown by hardness data and Young's modulus, the mechanical strength of the film is similar to oxide and one order of magnitude higher than that of polymeric films. Stress hysteresis is < 20 MPa after 6 cycles to 450°C and no structural or phase transition is observed at these conditions. Figure 1.

Adhesion to different materials and the ability to withstand CMP are two critical structural issues. Film adhesion was investigated by mechanical stud pull testing and ASTM tape test. Adhesion to TaN, Ta, SiO<sub>2</sub>, SiN, Ti, and TiN is very good, both when measured as-deposited and after temperature cycling (7 cycles at 400°C). Adhesion was also evaluated after direct CMP

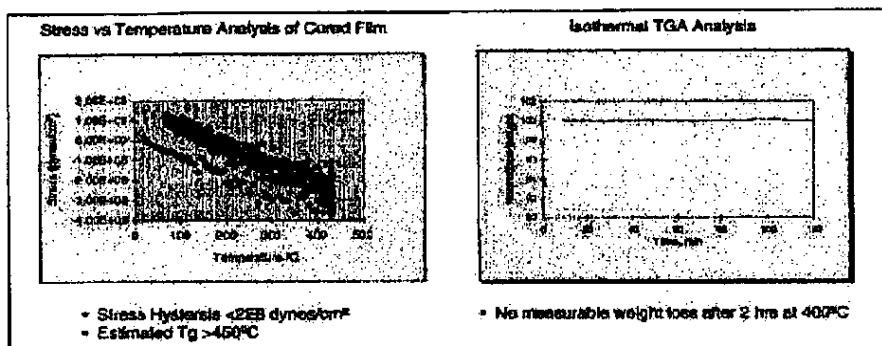


Figure 1  
Thermal properties  
(isothermal TGA)

of the film and after CMP of copper on the material. No delamination was observed in either instance. No adhesion layers or underlayers were required to achieve these results. A film thickness of >1.5µm can be deposited without any cracking or delamination. The electrical properties of the film, such as breakdown voltage and leakage current, were also investigated and show similar values compared to standard PE-TEOS oxide, Table 3.

As deposited, the films are stable, but a furnace anneal is required to achieve the lowest dielectric constant value. The anneal can be performed in a vacuum furnace under nitrogen (or forming gas) atmosphere. The purpose of the anneal is to out-gas the un-reacted low molecular weight species. The shrinkage of post cured films is <1% for temperature cycles up to 450°C.

#### ELECTRICAL PERFORMANCE

The Black Diamond film's in-plane dielectric constant was measured by Hg probe and has a bulk  $k$  value of 2.7. The line-to-line capacitance was obtained by in-house electrical test of an integrated Black-Diamond-Cu single damascene structure. Capacitance measurements from inter-digitated comb structures show a 28% reduction in capacitance for the fully integrated film compared to a similar structure using standard  $\text{SiO}_2$ . Figure 2. This equates to approximately  $k=2.9$  after integration, including resist ash, solvent clean, and other processing steps.

Black Diamond is an amorphous material and should have isotropic behavior. The interdigitated comb capacitance measurements are in agreement with the Hg probe measurement, and confirm the isotropic nature of this film. Leakage current was <5E-8 A/cm² at 1V, and the breakdown field was >2.5MV/cm. Thus, the film provides a significant reduction in capacitance, while meeting electrical requirements for dielectric isolation.

#### FILM INTEGRATION

One of the major challenges for early low  $k$  materials was the lack of integration knowledge. The ability to quickly evaluate material interactions with different process modules is an important tool for tuning the film composition and characteristics. In the case of this new film, the company's Process Sequence Integration (PSI) group collaborated with the dielectric deposition, dielectric etch, CMP, and metal deposition product groups to develop and demonstrate the successful integration of Black Diamond in Cu damascene structures.

Trench and via etching was accomplished using a high-density plasma dielectric etcher. The dielec-

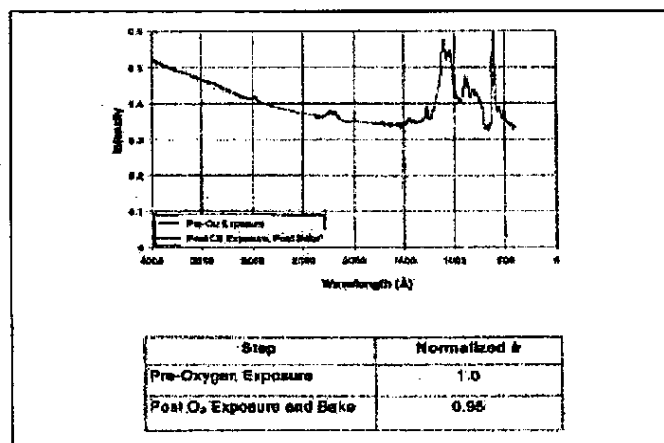
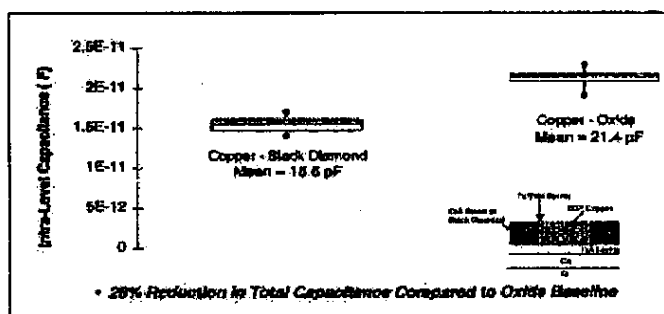


Figure 2 (top)  
Black Diamond Intra-Level  
Capacitance Comparison

Figure 3 (above)  
Black Diamond Compatibility with  
Low Pressure, Zero Bias O<sub>2</sub> Ash

tric etch baseline recipe was transferred to Black Diamond, achieving good profiles. Post-etch clean used resist ashing followed by solvent strip. Black Diamond was found to be compatible with post-etch solvent cleans such as EKC 525 and ACT 970, among others, with no chemical changes and no delamination or swelling issues. No compositional changes were observed in the FTIR spectra, Figure 3, after the etch and photoresist removal sequence. A TaN barrier layer and Cu seed layer was deposited by Ion Metal Plasma (IMP) technology and copper fill was accomplished using the company's electrochemical

deposition technology.

Copper polishing was performed in the company's CMP tool to complete the single-damascene structure, Figure 4.

Figure 5 shows the electrical line-width for trenches varying from 0.34 to 30 micron. The CMP performance of the Black Diamond film is very consistent and was found to be equivalent to that of oxide-Cu damascene structures. The CMP baseline process for Cu-SiO<sub>2</sub> interconnect was transferable to Cu-Black Diamond. No issues with metal delamination or dielectric deformation were observed.

The resultant line-to-line capacitance from the integrated structure was shown earlier in Figure 1.

Figure 6 shows a dual damascene integrated structure with Black Diamond. The integration was achieved with a process sequence consisting of the company's dielectric etch, Barrier and Seed layer (IMP Ta/TaN (PVD);

Cu (PVD)); ElectroChemical plating (Cu, ECP) and Cu CMP systems. The process sequence resulted in relatively easy and robust integration.

Our testing found that Black Diamond facilitates integration by avoiding many of the issues associated with carbon-based materials, such as inability to use O<sub>2</sub> resist ashing. The Si-O based film is compatible with O<sub>2</sub> resist strip and has excellent adhesion to different surfaces. The film is also compatible with the temperature requirements of advanced interconnect modules. Overall the product enables ease of integration matched with established manufacturing processes.

#### MANUFACTURABILITY

Manufacturing worthiness is critical to low  $k$  technology. The key factors that affect this are cost, environmental safety and health, low particulates, and ease of operation. The Black Diamond film maintains a low total cost

Figure 4  
Integrated Structure with Black  
Diamond and Copper Fill

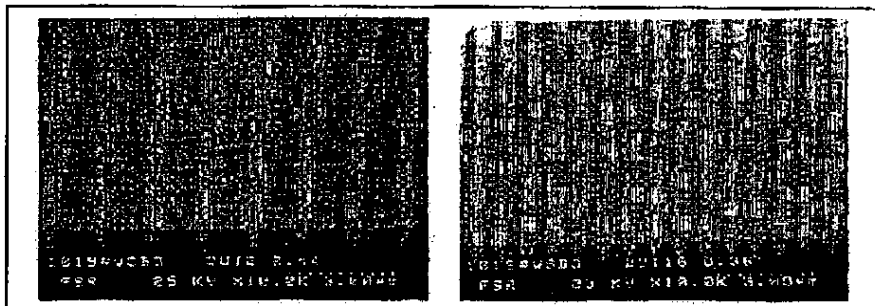


Figure 5  
Electrical line-width consistency  
in up to 30micron lines showing  
compatibility of Black Diamond  
with CMP

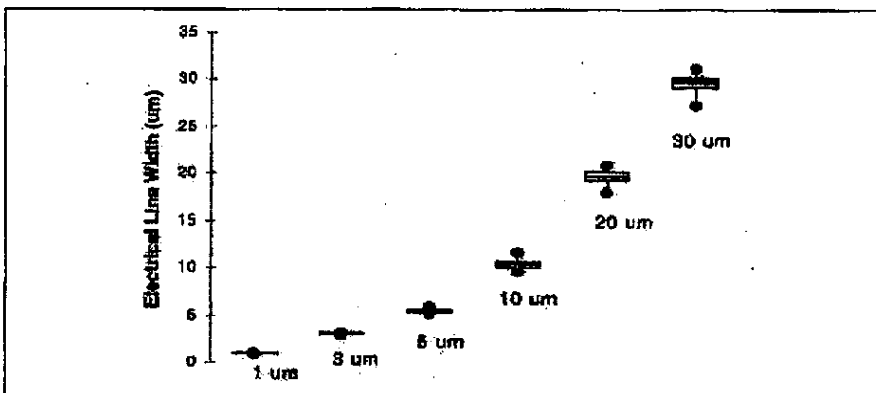
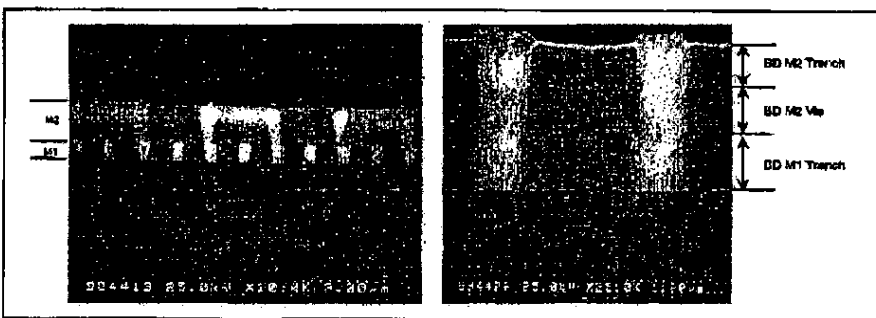


Figure 6  
Black Diamond dual damascene  
integration structure



of ownership by using non-proprietary, industry standard chemicals; customers also have a choice of high throughput wafer handling platforms. The deposition chambers are cleaned using a remote plasma clean technology that eliminates PFC exhaust emissions, extends the lifetime of the process kit, and prevents any residue accumulation in the chamber. This translates into a repeatable, cost effective process with low particulates.

#### CONCLUSION

Black Diamond is the first-generation product of the Black Diamond CVD family of low  $k$  products. This film exhibits the thermal, mechanical, and electrical film properties to be a promising low  $k$  material ( $k < 2.7$ ) for IMD applications. The material has been successfully integrated into single and dual damascene structures using a standard equipment set. The electrical tests indicate a substantial reduction in the capacitance as compared to silicon oxide. This technology provides a CVD film capable of meeting advanced device requirements in a production worthy method.

#### ABOUT THE AUTHORS

Wai-Pan Yau received his Ph.D. in Materials Science from the University of California at Berkeley in 1992. From 1992 to 1994, he worked for IMF, Inc. as a senior process development engineer on technology development of various CMOS and BiCMOS processes. In 1994, he joined Applied Materials to work on technology development of various dielectrics. He is currently working as a senior technology manager in the Planarization and Dielectric Deposition Group.

Peter Lee received his BS in Chemical Engineering and Materials Science from the University of California at Berkeley, and his

Ph.D. in Chemical Engineering from the University of Minnesota. He joined Applied Materials in 1988. He invented the SACVD process in 1989, and has since worked on PECVD silane, TEOS and FSG process development. He currently is Senior Manager of Key Account Technology for Applied Materials' Low  $k$  Product Unit.

Mahul Nair received his Ph.D. from Rensselaer Polytechnic Institute for his work on Chemical Vapor Deposition of Copper. He is a Senior Process Engineer with the Process Sequence Integration group at Applied Materials. His current focus is on Cu integration with oxide and low  $k$  dielectric materials.

Ben Pang is the Global Product Manager for the Low  $k$  Strategic Product Unit. Before joining Applied Materials in 1989, he worked as a process engineer at IBM and SRI International. Mr. Pang has a M.S. in Chemical Engineering from UCLA and a BS in Chemical Engineering from UC-Berkeley.

#### IF YOU HAVE ANY ENQUIRIES REGARDING THE CONTENT OF THIS ARTICLE, PLEASE CONTACT:

Betty Newboe

Applied Materials Inc.

2881 Scott Boulevard

M/S 1918

Santa Clara

CA 95050

USA

Tel: +1 (408) 563-0647

Fax: +1 (408) 886-2855

E-mail: Betty\_X\_Newboe@amat.com

[Reader Ref. 37]